AD-A255 862

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

DTIC ELECTE SEP 25 1992 S D C

1a REPORT SECURITY CLASSIFICATION: Unclassified

1b

2a SECURITY CLASSIFICATION AUTHORITY

2b DECLASSIFICATION / DOWNGRADING SCHEDULE

3 DISTRIBUTION / AVAILABILITY OF REPORT

4 PERFORMING ORGANIZATION REPORT NUMBER(S): 15

5 MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION: NIST

6b OFFICE SYMBOL (If applicable)

7a NAME OF MONITORING ORGANIZATION: ONR

6c ADDRESS (City, State, and ZIP Code)

7b ADDRESS (City, State, and ZIP Code):
Code 1131
800 N. Quincy Street
Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION: ONR

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-90-F-0011

8c. ADDRESS (City, State, and ZIP Code)

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT NO

11 TITLE (Include Security Classification)

Twin Quintuplets in CVD Diamond

12 PERSONAL AUTHOR(S) D. Shechtman, A. Feldman, J.L. Hutchison

13a. TYPE OF REPORT	13b. TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Interim	FROM ______ TO ______	1992-Aug-26	6

16 SUPPLEMENTARY NOTATION

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

This document has been approved for public release and sale: its distribution is unlimited.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The atomic structure of twin quintuplets in a chemical vapor deposited (CVD) diamond film was investigated by high resolution transmission electron microscopy (HRTEM). We conclude that the twin quintuplets have two main morphologies. The first consists of four $\Sigma=3$ twin boundaries and one $\Sigma=81$ twin boundary. The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate a 7.35° misfit angle between a set of {111} planes on opposite sides of the boundary. In the second case, the 7.35° misfit angle is accommodated by two or more grain boundaries that are tilted slightly more than the 70.53° tilt of a $\Sigma=3$ boundary. These grain boundaries and the conventional diamond lattice twin boundaries are the only types of boundaries that we have observed in CVD diamond.

92 9 24 017

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL

22b TELEPHONE (Include Area Code) | 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

OFFICE OF NAVAL RESEARCH

Contract N00014-90-F-0011

R&T Project No. IRMT 025

TECHNICAL REPORT No. 15

TWIN QUINTUPLETS IN CVD DIAMOND

D. Shechtman*, A. Feldman, J.L Hutchison**

submitted to

Proceedings of the SPIE

National Institute of Standards and Technology

Ceramics Division

Gaithersburg, MD 20899

August 26, 1992

*Visiting scientist at the Johns Hopkins University and at NIST from the Technion, Israel.
** University of Oxford, England

Twin quintuplets in CVD diamond

D. Shechtman*

Technion, Haifa, Israel

J.L. Hutchison

University of Oxford, UK

A. Feldman

National Institute of Standards and Technology

ABSTRACT

The atomic structure of twin quintuplets in a chemical vapor deposited (CVD) diamond film was investigated by high resolution transmission electron microscopy (HRTEM). We conclude that the twin quintuplets have two main morphologies. The first consists of four $\Sigma=3$ twin boundaries and one $\Sigma=81$ twin boundary. The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate a 7.35° misfit angle between a set of $\{111\}$ planes on opposite sides of the boundary. In the second case, the 7.35° misfit angle is accommodated by two or more grain boundaries that are tilted slightly more than the 70.53° tilt of a $\Sigma=3$ boundary. These grain boundaries and the conventional diamond lattice twin boundaries are the only types of boundaries that we have observed in CVD diamond.

1. INTRODUCTION

The defect structure of chemical vapor deposited (CVD) diamond has been studied in recent years as the technology to grow diamond has developed[1-7]. Most of these defects were found to be twins of well defined orders, $\Sigma=3$, 9, 27 and 81. Analyses by transmission electron microscopy (TEM) and by high resolution TEM (HRTEM) have revealed the fine structure of the twins and has shed light on their formation and their role in the growth of CVD diamond[8-10]. In addition to cataloging the types of twins observed, several authors have examined formations typical of twin interactions. Among these are twin quintuplets which have been found both near the center of grain cross-sections and at the periphery of grains. It is the purpose of this article to define some of the crystallographic parameters of these twin quintuplets and to describe how these defects influence the growth and morphology of CVD diamond.

2. EXPERIMENTAL

The film used in this study was prepared by microwave plasma CVD. Details of the deposition have been described previously and will not be discussed here[8]. The film was placed

*Visiting scientist at the Johns Hopkins University and at NIST

between TEM grids and thinned by ion milling for the HRTEM study. The high resolution transmission electron microscope used has a point resolution of 0.16 nm. All of the diamond grains studied were tilted so as to align a [110] direction parallel to the electron beam. Under this condition, each part of the diamond specimen contained two {111} planes and one (002) plane in an edge-on position relative to the electron beam axis. Atomic resolution images were recorded at 500K magnification close to the Scherzer defocus.

3. RESULTS AND DISCUSSION

3.1 Diffraction from twins

A diffraction pattern from a multiply-twinned diamond crystal is shown in Figure 1. The pattern is composed of five diffraction pattern sets, each with a [110] zone axis. The discrete patterns are rotated 70.53° relative to one another. This results from the rigid structural characteristic of the diamond lattice which allows only five sets of twins to exist in each [110] zone. There is, however, some slack in this rigidity which we discuss below. An analysis of the diffraction pattern from one pair of $\Sigma=3$ related twins in CVD diamond has been given elsewhere[8].

3.2 Twin quintuplets

The twins, whose boundaries are observed in an edge-on position, are in most cases present throughout the specimen. The twinning frequency is small at the center of the grain and higher toward the periphery of the grain. The twins intersect one another to form $\Sigma=3$ boundaries and boundaries of higher order, namely $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$[9,10]. In some cases more than two twins intersect and an important case is that of five intersecting twins which we call a twin quintuplet. It has been suggested[9] that a twin quintuplet is an important nucleation site for new planes in CVD diamond, but not all twin quintuplets serve such a central role. Our observations indicate that in addition to the main twin quintuplets near the center of a grain that may manifest themselves in the final morphology of the crystal, there are numerous secondary twin quintuplets. Several of these can be found in each [110] section of a diamond crystal.

The core of a twin quintuplet is a line defect called a quintuplet axis. In a main quintuplet, the quintuplet axis frequently propagates from the center of the diamond crystal to its surface. This axis is usually viewed in an end-on position in the HRTEM images. At the surface, the quintuplet axis emerges as the apex of a five sided pyramid. The sides of this pyramid are usually {111} planes. A maximum number of twelve main quintuplet axes can form at the center of a diamond crystal, thus, creating an icosahedrally shaped diamond crystal[8]. The icosahedron is not perfectly regular because of the 7.35° misfit angle. In some instances a quintuplet axis does not emerge from the surface of the grown crystal, thus remaining a local internal phenomenon.

A discussion of the crystallography of the twin quintuplets follows. Because the twinning angle of a $\Sigma=3$ boundary is 70.53°, there can be no more than four $\Sigma=3$ boundaries in a twin quintuplet. Thus, an angle of 7.35° would remain between {111} planes in a pair of the twins, and this angle we call a misfit angle because it results in a noncoherent twin boundary. Our observations indicate that the lattice deals with this misfit in one of two ways.

Twin Quintuplet Type I: In this case the misfit angle creates a $\Sigma=81$ twin boundary which is a fourth order twin boundary; the twinning angle is 77.88°. The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate the 7.35° misfit angle between a set of {111} planes on opposite sides of the boundary. This case has been documented previously[9,10], where it was shown that the boundary thus formed can transform into a $\Sigma=3$ boundary by emitting a series of dislocations[9]. An example of a Type I twin quintuplet is given in Figure 2. The inset illustrates the misfit angle that forms the $\Sigma=81$ boundary. In addition, the {111} planes near the quintuplet axis are marked. An example of a similar twin quintuplet can be seen at the upper left corner of the micrograph (marked with a circle). The orientation and crystallographic character of both examples are identical.

Twin Quintuplet Type II: This case differs from Type I in that the 7.35° misfit angle does not result in a $\Sigma=81$ boundary. Instead, the misfit is accommodated by more than one of the quintuplet boundaries to form grain boundaries whose tilt angles are slightly more than the 70.53° tilt angle of a $\Sigma=3$ twin boundary. Because the misfit angle of one of these boundaries does not have a determined value, we consider the boundary to be non-crystallographic. In Figure 3, the 7.35° misfit angle is divided so as to create two non-crystallographic boundaries. These form between the crystallite pairs (B,C) and (A,E). The other boundaries, between the pairs (A,B), (D,E) and (C,D), are of the $\Sigma=3$ type. The inset in Figure 3 illustrates the twin quintuplet and the division of the misfit angle. Several {111} plane traces are also marked on the micrograph. Near mirror symmetry is clearly observed on the two sides of the (A,B) $\Sigma=3$ boundary. This symmetry is probably caused by nearly identical strain patterns on both sides of the (A,B) twin boundary. The characteristic shape that emerges from this type of twin quintuplet is rather abundant in CVD diamond crystals. Thus, the (A,B) $\Sigma=3$ twin boundary is not only a crystallographic mirror plane for the neighboring twins, but also a morphological near mirror plane for the characteristic "Coat of Arms" shape outlined by the high order twins on both of its sides.

In addition to the situation discussed above, we have observed a misfit angle divided into three parts in other micrographs containing twin quintuplets.

4. CONCLUSION

Atomic resolution electron microscopy of a CVD diamond film was used to determine the crystallography and morphology of twin quintuplets. Two basic types of twin quintuplet centers were revealed and the twin boundaries around them studied. The first type consists of four $\Sigma=3$ twin boundaries and one $\Sigma=81$ twin boundary. The $\Sigma=81$ twin boundary contains the dislocations needed to accommodate a 7.35° misfit angle between a set of {111} planes on opposite sides of the boundary. In the second type, the 7.35° misfit angle is accommodated by two or more grain boundaries that are tilted slightly more than the 70.53° tilt of a $\Sigma=3$ boundary.

5. ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research.

6. REFERENCES

1. B.E. Williams and J.T. Glass, J. Mater. Res. 4, 373 (1989)

2. J. Narayan, J. Mater. Res. 5, 2414 (1990)
3. B.E. Williams, J.T. Glass, R.F. Davis, K. Kobashi and K.L. More, Proc. 1st Int. Symp. Diamond and Diamond Like Films, J.P. Dismukes, editor 202 (1989).
4. G-H.M. Ma, Y.H. Lee and J.T. Glass, J.Mater. Res. 5, 2367 (1990).
5. J. Narayan, A.R. Srivatsa, M. Peters S. Yokota and K.V. Ravi, Appl. Phys. Lett. 53,1823(1988).
6. B.E. Williams, H.S. Kong and J.T. Glass, J. Mater. Res. 5, 801(1990).
7. K. Kobashi, K. Nishimura, K. Miyata, Y. Kawate, J.T. Glass and B.E. Williams, SPIE Diamond Optics, 969, 159(1988).
8. D. Shechtman, E.N Farabaugh, L.H. Robins, A. Feldman and J.L. Hutchison, SPIE Vol. 1534 Diamond optics IV (1991).
9. D. Shechtman, J.L Hutchison, L.H. Robins, E.N. Farabaugh, and A. Feldman, to be published.
10. D. Shechtman, A. Feldman, M.D. Vaudin, and J.L Hutchison, to be published.

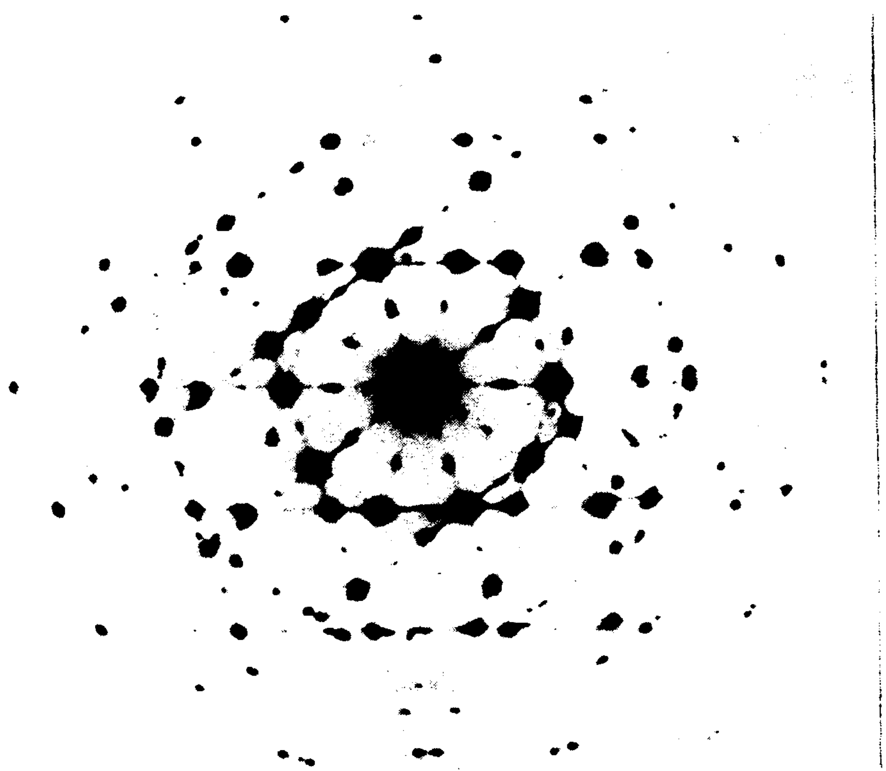

Fig. 1. A diffraction pattern taken from a whole diamond crystal is composed of five twin diffraction variations.

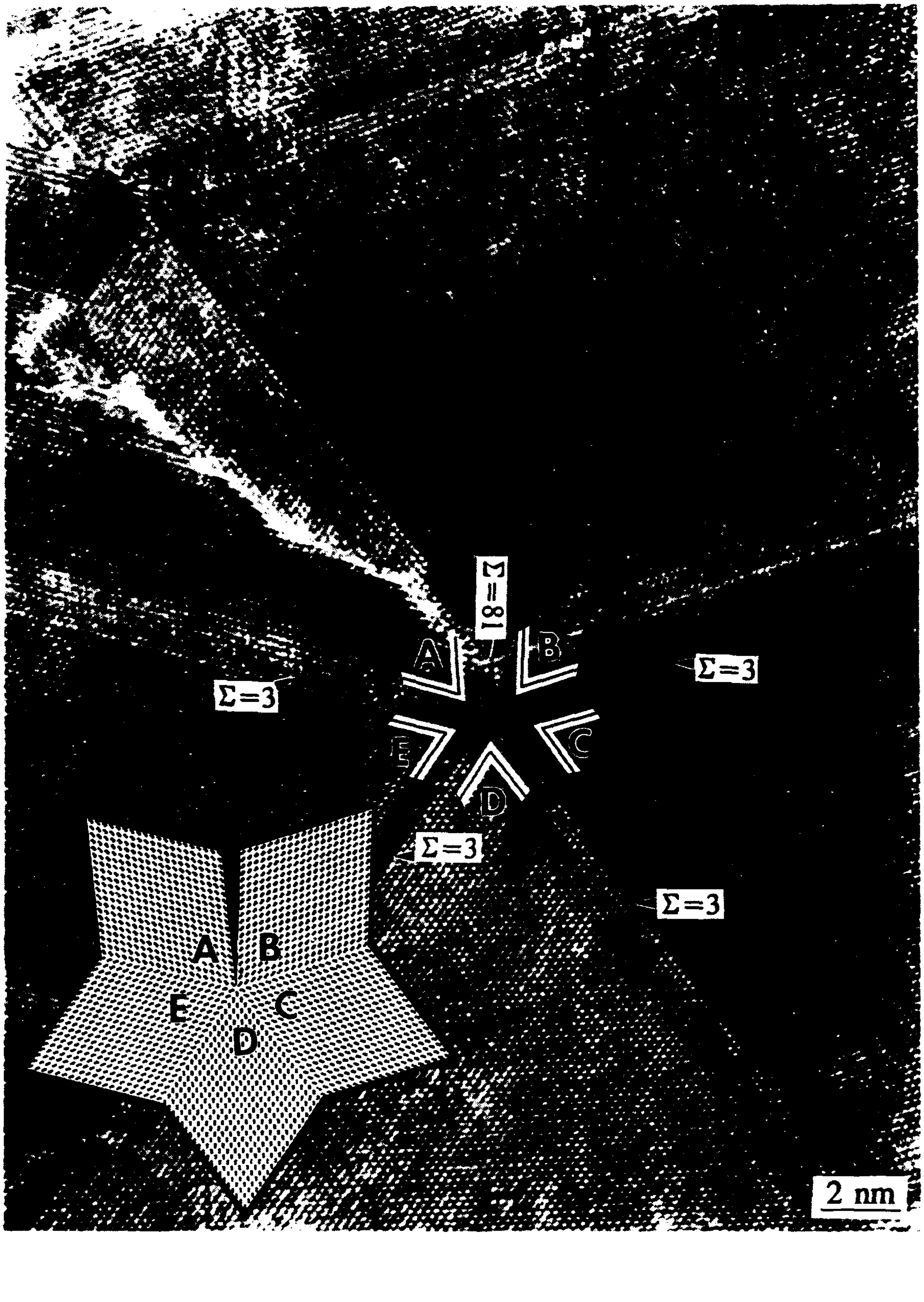

Fig. 2. A Type I twin quintuplet. The misfit angle creates a $\Sigma=81$ twin boundary.

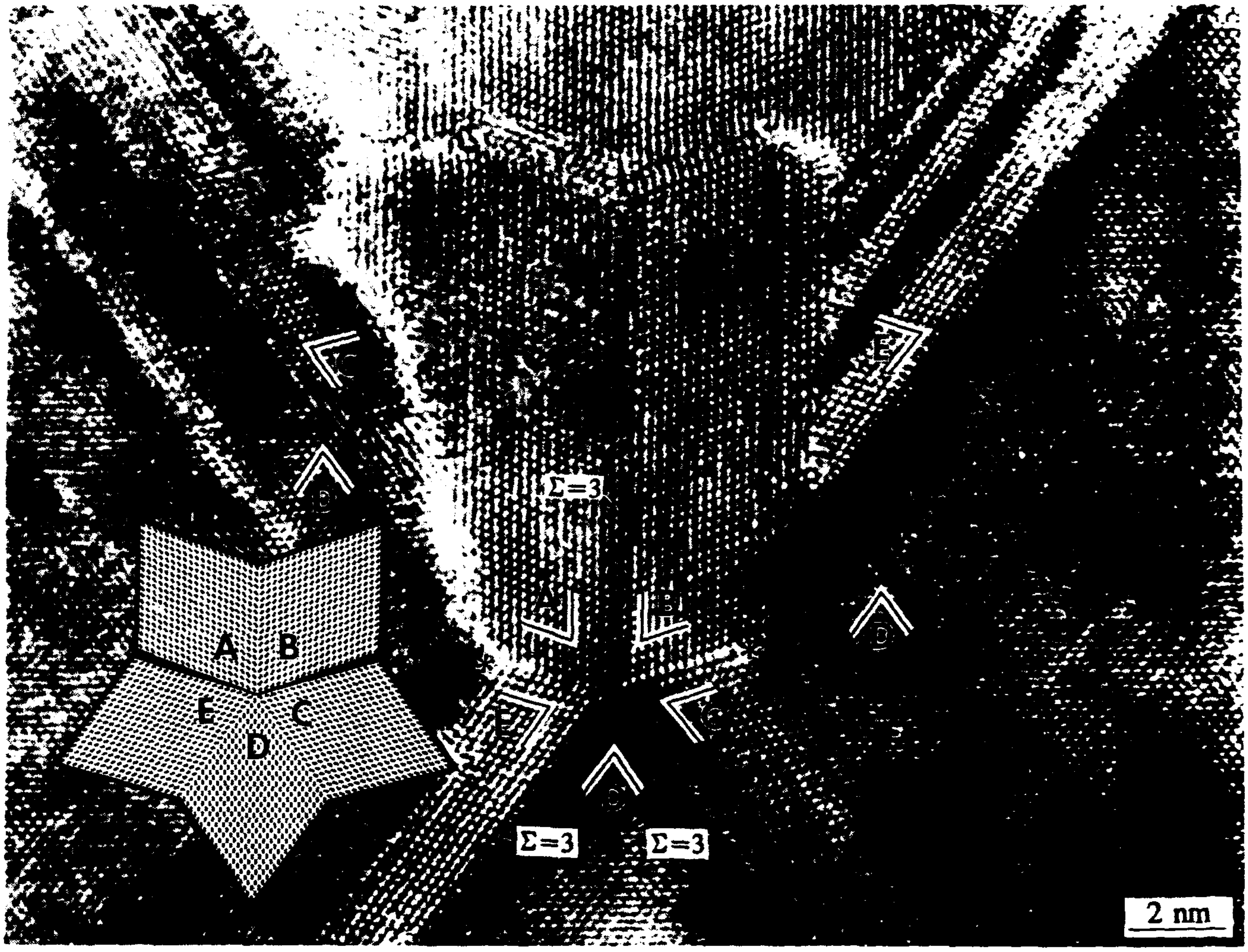

Fig. 3. A Type II twin quintuplet. In this example the misfit angle is divided into two grain boundaries. Between the points market * a series of high order twin boundaries form a "Coat of Arms" shape, characteristic of Type II.

27 June 1992

Distribution List

Mr. James Arendt
Hughes Aircraft Company
8433 Fallbrook Avenue 270/072
Canoga Park, CA 91304
(838) 702-2890

Mr. Larry Blow
General Dynamics
1525 Wilson Blvd., Suite 1200
Arlington, VA 22209
(703) 284-9107

Mr. Ellis Boudreaux
Code AGA
Air Force Armament Laboratory
Eglin AFB, FL 32542

Dr. Duncan W. Brown
Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810-4131

Dr. Mark A. Cappelli
Stanford University
Mechanical Engineering Department
Stanford, CA 94305
(415) 723-1745

Dr. R. P. H. Chang
Materials Science & Engineering Dept.
2145 Sheridan Road
Evanston, IL 60208
(312) 491-3598

Defense Documentation Center
Cameron Station
Alexandria, VA 22314
(12 copies)

Dr. Bruce Dunn
UCLA
Chemistry Department
Los Angeles, CA 90024
(213) 825-1519

Dr. Al Feldman
Leader, Optical Materials Group
Ceramics Division
Materials Science & Engineering Lab
NIST
Gaithersburg, MD 20899
(301) 975-5740

Dr. John Field
Department of Physics
University of Cambridge
Cavendish Laboratory
Madingley Road
Cambridge CB3 OHE
England
44-223-3377333 Ext. 7318

Dr. William A. Goddard, III
Director, Materials and Molecular
Simulation Center
Beckman Institute
California Institute of Technology
Pasadena, CA 91125
(818) 356-6544 Phone
(818) 568-8824 FAX

Dr. David Goodwin
California Institute of Technology
Mechanical Engineering Dept.
Pasadena, CA 91125
(818) 356-4249

Dr. Kevin Gray
Norton Company
Goddard Road
Northboro, MA 01532
(508) 393-5968

Enclosure (1)

Mr. Gordon Griffith
WRDC/MLPL
Wright-Patterson AFB, OH 45433

Dr. H. Guard
Office of Chief of Naval Research
(ONR Code 1113PO)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Alan Harker
Rockwell Int'l Science Center
1049 Camino Dos Rios
P.O. Box 1085
Thousand Oaks, CA 91360
(805) 373-4131

Mr. Stephen J. Harris
General Motors Research Laboratories
Physical Chemistry Department
30500 Mound Road
Warren, MI 48090-9055
(313) 986-1305 Phone
(313) 986-8697 FAX
E-mail: SHARRIS@GMR.COM

Mr. Rudolph A. Heinecke
Standard Telecommunication
Laboratories, Ltd.
London Road
Harlow, Essex CM17 9MA
England
44-279-29531 Ext. 2284

Dr. Kelvin Higa
Code 3854
Naval Weapons Center
China Lake, CA 93555-6001

Dr. Curt E. Johnson
Code 3854
Naval Weapons Center
China Lake, CA 93555-6001
(619) 939-1631

Dr. Larry Kabacoff (Code R32)
Officer in Charge
Naval Surface Weapons Center
White Oak Laboratory
10901 New Hampshire
Silver Spring, MD 20903-5000

Mr. M. Kinna
Office of Chief of Naval Research
(ONT Code 225)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Paul Klocek
Texas Instruments
Manager, Advanced Optical Materials Br.
13531 North Central Expressway
P.O. Box 655012, MS 72
Dallas, TX 75268
(214) 995-6865

Ms. Carol R. Lewis
Jet Propulsion Laboratory
4800 Oak Grove Drive
Mail Stop 303-308
Pasadena, CA 91109
(818) 354-3767

Dr. J.J. Mecholsky, Jr.
University of Florida
Materials Science & Engineering Dept.
256 Rhines Hall
Gainesville, FL 32611
(904) 392-1454

Dr. Russell Messier
202 Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802
(814) 865-2326

Mr. Mark Moran
Code 3817
Naval Weapons Center
China Lake, CA 93555-6001

Mr. Ignacio Perez
Code 6063
Naval Air Development Center
Warminster, PA 18974
(215) 441-1681

Mr. C. Dale Perry
U.S. Army Missile Command
AMSMI-RD-ST-CM
Redstone Arsenal, AL 35898-5247

Mr. Bill Phillips
Crystallume
125 Constitution Drive
Menlo Park, CA 94025
(415) 324-9681

Dr. Rishi Raj
Cornell University
Materials Science & Engineering Dept.
Ithaca, NY 14853
(607) 255-4040

Dr. M. Ross
Office of Chief of Naval Research
(ONR Code 1113)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Rustum Roy
102A Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802
(814) 863-7040 FAX

Dr. James A. Savage
Royal Signals & Radar Establishment
St. Andrews Road
Great Malvern, Worcs WR14.3PS
England
01-44-684-895043

Mr. David Siegel
Office of Chief of Naval Research
(ONT Code 213)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Keith Snail
Code 6520
Naval Research Laboratory
Washington, DC 20375
(202) 767-0390

Dr. Y. T. Tzeng
Auburn University
Electrical Engineering Department
Auburn, AL 36849
(205) 884-1869

Dr. Terrell A. Vanderah
Code 3854
Naval Weapons Center
China Lake, CA 93555-6001
(619) 939-1654

Dr. George Walrafen
Howard University
Chemistry Department
525 College Street NW
Washington, DC 20059
(202) 806-6897/6564

Mr. Roger W. Whatmore
Plessey Research Caswell Ltd.
Towcester Northampton NN128EQ
England
(0327) 54760

Dr. Charles Willingham
Raytheon Company
Research Division
131 Spring Street
Lexington, MA 02173
(617) 860-3061

Dr. Robert E. Witkowski
Westinghouse Electric Corporation
1310 Beulah Road
Pittsburgh, PA 15235
(412) 256-1173

Dr. Aaron Wold
Brown University
Chemistry Department
Providence, RI 02912
(401) 863-2857

Dr. Walter A. Yarbrough
260 Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802
(814) 865-2326

Mr. M. Yoder
Office of Chief of Naval Research
(ONR Code 1114SS)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Robert Pohanka (Code 1131)
Office Of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Dr. David Nelson (Code 1113)
Office Of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Dr. Robert W. Schwartz (Code 38505)
Naval Weapons Center
China Lake, CA 93555